

**Mechanism of the electrodeposition of Ag and Ag-Au alloys on n-Si (111) and properties of the deposits.**

**K. Márquez, G. Staikov, J.W.Schultze**  
Institut für Physikalische Chemie und Elektrochemie  
Heinrich-Heine-Universität  
Düsseldorf, GERMANY

The electrochemical deposition of metals and alloys on semiconductor substrates plays an increasingly important role in many modern technologies. Under appropriate experimental conditions, metal deposition is achieved even on substrates of complex geometries, which is of great significance for micro-structuring. However, the structure and properties of the resulting metal and alloy films are strongly dependent on the mechanism of nucleation and growth. Therefore a detailed understanding of the processes occurring during electrodeposition is crucial for obtaining high quality deposits<sup>1</sup>.

In this contribution the nucleation and growth mechanisms during the deposition of Ag and Ag-Au alloys on H-terminated n-Si (111) from cyanide solutions (pH 14) will be presented and compared with results obtained on glassy carbon electrodes. The initial stages of metal deposition have been studied using classical chronoamperometric experiments combined with AFM, STM and SEM measurements. Some specific aspects of the existing theories for nucleation and growth<sup>2,3</sup> applied to the studied systems will be discussed.

Figure 1 shows typical current-time curves for the deposition of Ag from a 5mM Ag(CN)<sub>2</sub><sup>-</sup> solution, in which deposition takes place at relatively high overpotentials ( $U_{dep} < U_{fb} < U_{eq}$ ). In figure 2 an AFM image showing silver clusters deposited at -800mV (vs SHE) is presented. Silver crystallites of different sizes can be observed, which corresponds to a progressive nucleation. However, at potentials more negative than -900mV instantaneous nucleation takes place (Figure 3). Quantitative analysis of experimental transients was performed using a nonlinear least square fitting procedure developed by L. Heerman and A. Tarallo<sup>4</sup>. The fitting program is based on the Levenberg-Marquardt algorithm with the nucleation site density and the nucleation rate constant as fitting parameters. Differences between the values for  $N_0$  calculated from the transient measurements and the actual observed number of clusters using AFM or SEM have also been studied.

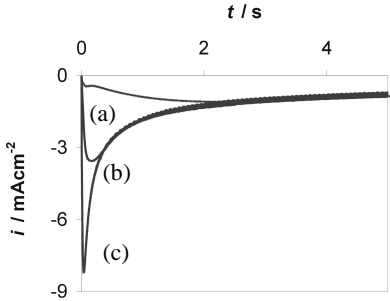
The electronic behavior of the metal/silicon and alloy/silicon contacts was investigated using capacity and current-potential measurements. Figure 4 shows the ideal Schottky behavior of a solid state n-Si/Ag contact. A high-quality junction with a low density of interface states was obtained.

With the use of XPS, AFM, EDX and XRD techniques, some physical and structural properties of the deposited silver and alloy films have been determined. In figure 5 an X-ray photoelectron spectrum of an alloy containing 35% Ag and 65% Au is shown. The presence of gold improves significantly the adhesion of the deposit to the silicon surface, when compared to silver alone. XRD measurements proved the formation of a polycrystalline fcc alloy with a preferential (111) orientation.

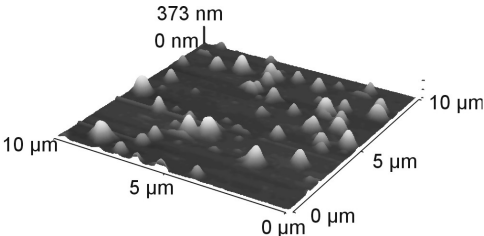
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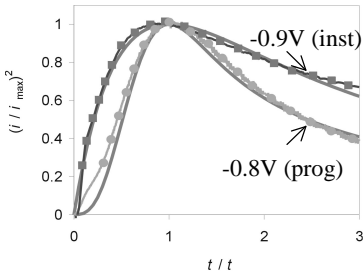
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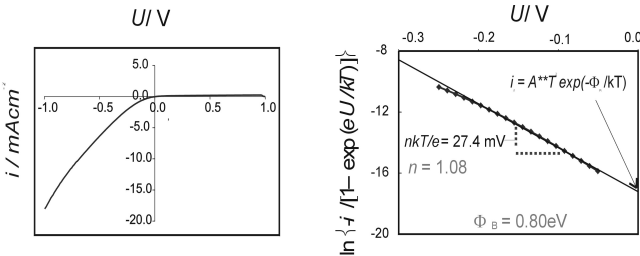
**Fig. 1.** Current-time curves for the deposition of Ag onto n-Si(111) from a 5mM Ag(CN)<sub>2</sub><sup>-</sup> solution at: (a) -800mV; (b) -870mV; (c) -900 mV(vs SHE).



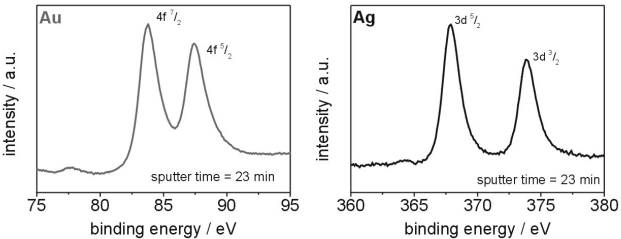
**Fig. 2.** 10 x 10 μm AFM image of silver clusters on n-Si(111). Deposition potential -800mV; deposition time: 20s.



**Fig. 3.** Reduced-variable plots for the deposition of silver on n-Si (111) at -800 mV and -900mV. The theoretical curves for instantaneous and progressive nucleation are also shown.



**Fig. 4.** Current-potential curve for a solid state n-Si/Ag junction fabricated by electrochemical deposition. The inverse slope of 27.4 mV corresponds to an ideality factor of 1.06. The barrier height was determined to be  $\Phi_B = 0.8$  eV.



**Fig. 5.** X-ray photoelectron spectrum of a Ag-Au alloy (35% Ag, 65% Au) deposited on n-Si(111) from a 5mM Ag(CN)<sub>2</sub><sup>-</sup> / 5mM Au(CN)<sub>2</sub><sup>-</sup> solution, using a double pulse routine.